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(54) Title: CATALYST FOR VAPOR PHASE OXIDATION OF ALKANE HYDROCARBONS

(57) Abstract

This invention relates to cation substituted catalysts based primarily upon vanadium pyrophosphate, useful in the oxidation of alkane hydrocarbons.

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TITLE
CATALYST FOR VAPOR PHASE OXIDATION
OF ALKANE HYDROCARBONS
FIELD OF THE INVENTION

5   This invention relates to cation substituted
catalysts, preferably in the form of solid solutions,
based primarily upon vanadium pyrophosphate, useful as
catalysts for the oxidation of alkane hydrocarbons,
particularly the production of maleic anhydride by the
10   vapor phase oxidation of n-butane.

BACKGROUND OF THE INVENTION

Maleic anhydride is used as a raw material for
products ranging from agricultural chemicals, paints,
paper sizing and food additives to synthetic resins. To
15   fill the high demand for this valuable chemical, a
variety of commercial processes have been developed, the
most successful of which involves the vapor phase
oxidation of n-butane to maleic anhydride in the
presence of a vanadium-phosphorus-oxygen (VPO) catalyst.
20   Since the development of this method in the 1970's,
research has continued to continuously improve the
reaction conditions and, particularly, the VPO
catalysts.

A review of the improvements made in this
25   technology is given by G. J. Hutchings, in Applied
Catalysis, Elsevier Science Publishers B. V. Amsterdam,
72(1991), pages 1-31. The preferred method of
preparation of VPO catalysts is the hydrochloric acid
digestion of V_2O_5 and H_3PO_4 in either an aqueous solvent
30   or non aqueous solvent, such as methanol, tetrahydro-
furan (THF) or isobutanol, followed by solvent removal
to give what is termed the catalyst precursor, which is
then activated by heating. Vanadium, phosphorus and
oxygen can form a large number of distinct compounds
35   which have been well characterized, e.g., $\alpha-VOPO_4$,

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γ-VOPO$_4$, VOHPO$_4$, (VO)$_2$P$_2$O$_7$, VO(PO$_3$)$_2$ and VO(H$_2$PO$_4$)$_2$, the
most active catalytic phase believed to be (VO)$_2$P$_2$O$_7$.
While the predominant oxide phase in VPO catalysis is
(VO)$_2$P$_2$O$_7$, the VPO catalysts are usually referred to as

5   "mixed oxides" in recognition of the probable presence
of other oxide phases. VPO catalysts have V:P atomic
ratios typically in the range of 1:1-1.2 and average,
bulk vanadium oxidation states in the range 4.0-4.3.
One of the major methods employed to improve the

10   performance of VPO catalysts involved the use of
promoters.

In general the methods of preparing promoted
catalysts are the same as those described for the
unpromoted catalysts. Promoter compounds can be added

15   either (a) together with the vanadium and phosphorus
compounds prior to the preparation of the catalyst
precursor, or (b) by impregnation of the catalyst
precursor prior to formation of the final catalyst by
heat treatment. Vanadium/phosphorus/silicon catalyst

20   compositions made in an organic medium are known. Also
known are processes for preparing high surface area VPO
catalysts. Such catalysts containing up to 0.2 mole,
per mole of vanadium, of a transition, alkali or
alkaline earth metal, for example, tantalum, titanium,

25   niobium, antimony, bismuth or chromium have also been
disclosed. An improved VPO catalyst containing the
promoter comprising silicon and at least one of indium,
antimony, and tantalum has also been taught.

A number of cations, e.g., Co, Fe, Li, Zn, Ce, Mn,

30   Sn and Lu, are believed to form solid solutions in
(VO)$_2$P$_2$O$_7$. U.S. Patent 4,337,173 discloses a promoted
VPO catalyst comprising a substitutional solid-solution
type crystalline oxide represented by the general
formula [(V$_{1-x-y-z}$Fe$_x$Cr$_y$Al$_z$)O]$_2$P$_2$O$_7$, wherein $0 \leq x \leq 0.40$,

35   $0 \leq y \leq 0.40$, $0 \leq z \leq 0.40$, and $x + y + z \leq 0.40$, which

has the same crystal structure as $(VO)_2P_2O_7$. Promoters which these authors propose could be in solid solution with the $(VO)_2P_2O_7$ phase appear to be effective in very low concentrations.

In spite of the progress in catalyst and process development over the years, a need still remains to continue to improve the VPO catalyst and it is to that end that this invention is directed.

SUMMARY OF THE INVENTION

The invention provides for an improved VPO catalyst for the oxidation of alkane hydrocarbons comprising a crystalline oxide of formula I through IV:

$$\text{I} \quad (V_{1-x-y}A_xB_yO)_2P_2O_{7\pm\delta}$$
$$\text{II} \quad (V_{1-x}A_xO)_2P_{2-y}B_yO_{7\pm\delta}$$
$$\text{III} \quad (V_{1-y}B_yO)_2P_{2-x}A_xO_{7\pm\delta}$$
$$\text{IV} \quad (VO)_2P_{2-x-y}A_xB_yO_{7\pm\delta}$$

wherein A is at least one of the cations selected from the group consisting of Sb, As, and Bi; B is at least one of the cations selected from the group consisting of Ge, Sb, Pb, Al, Ga, Tl, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, La, Hf, W, Re, Os, Ir, Pt, Au, Ho, Be, Mg, Ca, Sr, Ba, Ra, Li, Na, K, Rb, Cs, and the rare earths, including Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, Pa, U; δ is 0 to less than 0.5, and x and y are as follows:

in formula I: $0.7 \geq x > 0$ for each A,
                $0.7 \geq y > 0$ for each B, and
                $0.7 \geq (x+y) > 0$;

in formula II: $0.7 \geq x > 0$ for each A, and
                $1.0 \geq y > 0$ for each B;

in formula III: $1.0 \geq x > 0$ for each A, and
                $0.7 \geq y > 0$ for each B; and

in formula IV: $1.0 > x > 0$ for each A,
                $1.0 > y > 0$ for each B, and
                $1 \geq (x+y) > 0$.

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The catalyst in accordance with this invention is believed to provide increased oxygen capacity in the catalyst's crystal lattice, i.e., the mobile or "reactive" oxygen contained in the catalyst. In the
5 case of the oxidation of n-butane, the catalyst in accordance with this invention is believed to be selective to maleic anhydride and/or to provide increased selectivity towards maleic anhydride by the oxidation of n-butane in the absence of gas phase
10 oxygen. Increases in selectivity towards maleic anhydride by, for instance, an increase in the selective "reactive" oxygen in the crystalline lattice ultimately leads to overall improvements in the yields of maleic anhydride from the n-butane oxidation process.

15   BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a chart of the percent conversion of n-butane to maleic anhydride versus the number of n-butane pulses utilized in a pulsed micro-reactor generated as described in Example 29. The white box
20 represents a catalyst of the present invention, $(V_{0.9}Sb_{0.05}Fe_{0.05}O)_2P_2O_7$ prepared as described in Example 1. The black box represents $(VO)_2P_2O_7$ prepared as in Comparative Example A. The black diamond represents $(V_{0.9}Cr_{0.1}O_2)P_2O_7$ prepared as in Comparative
25 Example B. The white diamond represents $(V_{0.9}Cr_{0.05}Fe_{0.05}O)_2P_2O_7$ prepared as in Comparative Example C.

Figure 2 is a chart of the selectivity to maleic anhydride versus the number of n-butane pulses utilized
30 in a pulsed micro-reactor generated as described in Example 29. The white and black boxes and diamonds represent the same compounds as described above for Figure 1.

Figure 3 is a chart of the percent conversion of
35 n-butane to maleic anhydride versus the number of

n-butane pulses utilized in a pulsed micro-reactor for
spray dried catalyst with 10 wt % silica generated as
described in Example 39. The white box represents a
catalyst of the present invention,

5    $(V_{0.9}Sb_{0.05}Fe_{0.05}O)_2P_2O_7/SiO_2$ prepared as in Example 39.
The black box represents $(VO)_2P_2O_7/SiO_2$ prepared as in
Comparative Example E.

Figure 4 is a chart of the selectivity to maleic
anhydride versus the number of n-butane pulses utilized

10   in a pulsed micro-reactor for spray dried catalyst with
10 wt % silica generated as described in Example 39.
The white and black boxes represent the same compounds
as described above for Figure 3.

DETAILED DESCRIPTION OF THE INVENTION

15   The improved VPO catalyst of present invention as
described above as formula I through IV is made by a
process similar to that described in U.S. Patent
4,442,226, herein incorporated by reference, wherein the
vanadium is in the +5 oxidation state, such as in V_2O_5

20   or NH_4VO_3, and is initially reduced to a substantial
degree to the +4 oxidation state by reaction in either
an aqueous or organic liquid medium. The reductant can
comprise a soluble inorganic compound, such as a halide
acid, for example, concentrated hydrochloric acid; a

25   reduced acid of phosphorus, for example, H_3PO_3; or a
soluble organic compound, for example, formaldehyde,
ethylene glycol, or glycolic, oxalic, citric or tartaric
acid. In an organic medium, the preferred medium
herein, the reductant can comprise one or more alcohols

30   selected from such species as n-propyl, isopropyl,
n-butyl, isobutyl, and benzyl alcohols. The reduction
can be brought about by slurrying the pentavalent
vanadium compound in the liquid medium, followed by
heating under reflux for the time necessary to bring

35   about the reduction.

The improvement in the VPO catalyst of this
invention, which leads to enhanced productivity of
maleic anhydride, results from the introduction of
promoter AB into the $(VO)_2P_2O_7$ crystal structure,
5   preferably introduced in a specific order and chemical
form, i.e., solid solution, following the reduction step
in which the tetravalent vanadium is formed. As
indicated, the promoter cation moieties comprise at
least one of As, Sb and Bi with at least one of Ge, Sb,
10   Pb, Al, Ga, Tl, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y,
Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, La, Hf, W, Re, Os, Ir,
Pt, Au, Ho, Be, Mg, Ca, Sr, Ba, Ra, Li, Na, K, Rb, Cs,
and the rare earths, including Ce, Pr, Nd, Sm, Eu, Gd,
Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, Pa, U. The most
15   preferred combination is Sb and Fe.

The formulae used herein above to describe the
catalysts of this invention are intended to clarify that
the specific placement of the cation substituents in the
crystal lattice can vary. For example, the cations can
20   be placed in whole or in part on a vanadium site in the
crystal lattice, or the cations can be placed in whole
or in part on a phosphorus site. In any event, this
method of introduction of cation substituent into the
crystal lattice is distinguished from those in the art
25   where one or more cation substituents are post-deposited
on the surface of the VPO composition. X-ray
diffraction data, detailed below in the Examples, show
that many of the catalysts in accordance with this
invention crystallize as a vanadium pyrophosphate or
30   pyrophosphate-like structure.

Although not essential to the basic performance of
the improved catalyst of this invention, it is preferred
that the cation substituents be introduced into the
reaction medium as the inorganic salts, and not the
35   metal oxides. Thus, in the organic system, they can be

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added as a cation with an appropriate attendant anion, for example, an acetate, alkoxide, anhydrous halide or acetylacetonate.

Following substantial reduction of the +5 vanadium
5   to the tetravalent species and the introduction of the requisite promoters or promoter precursors, the catalyst precursor is formed by the addition of any commonly used appropriate phosphorus compound, for example, anhydrous phosphoric acid with the continued heating of the
10   resultant mixture under reflux to give the catalyst precursor composition that can be isolated by filtration, following cooling of the slurry to room temperature. This product is subsequently dried at about 125°C to about 200°C in a flowing inert
15   atmosphere, such as nitrogen, for approximately 12 hours. At this point, oftentimes it is a crystalline species having an x-ray diffraction pattern similar to that of $VO(HPO_4) \cdot 1/2H_2O$, the precursor to vanadium phosphate catalyst.

20   This catalyst precursor is then calcined and activated in a fluidized reactor to generate the active catalyst phase. A typical activation procedure is detailed below:

          25-390°C in air
25   390°C 1 hour in air
          390°C 1 hour in 1.5% butane/air
          390-460°C 20 minutes in 1.5% butane/air
          460-460°C 18 hours in 1.5% butane/air
          460-420°C in 1.5% butane air
30   420-360°C in 1.5% butane/air, and
          360°C-25°C in N_2.

This catalyst precursor is then formed into a convenient catalyst shape, for ultimate charge into a reactor, by pelletizing the catalyst typically at about
35   30,000 psi (2.07 X 10^8 Pa) or less, to form small disks

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and crushing the pellet through sieves. For fixed bed
reactor evaluations, typically a -40, +60 mesh is used
(U.S. Sieve Series). Optionally, one could blend the
resultant powder with 1-3% of a die lubricant and pellet
5   binder, such as graphite or Sterotex®, a hydrogenated
cottonseed oil, commercially available from Capital City
Products Company, Columbus, Ohio, before tabletting.

        For fluidized bed reactor use, however, catalysts
prepared in the above manner may not have the optimum
10   particle size range for such a reactor. Hence, they
must be formed in the correct particle size range.
Attrition by abrasion and/or fracture of the particles
is a frequent problem in fluidized reactors, which
necessitates the addition of a binder to the catalyst
15   particles. Excessive particle attrition in these
reactors is caused, for example, by particle-to-particle
contact, abrasion with bed walls and bed internals, as
well as distributor jet impingement and abrasion in
circulation conduits leading to and from the reactor
20   bed. High particle attrition contributes to product
contamination and catalyst loss, plugging of down stream
equipment, high filtration costs, and unstable
fluidization behavior such as channeling, slugging or
increased entrainment of reactants. The deleterious
25   effects of fluidized bed operations can be exacerbated
by high temperature conditions. These catalysts, by
themselves, cannot be formed in the correct particle
size range with sufficient mechanical strength to be
attrition resistant.
30   In addition to mechanical strength, particle shape
can also have an impact on attrition. Spheroidal
particles with smooth surfaces will have lower attrition
losses than particles with irregular shapes and rough
edges. Spheroidal is defined herein to include
35   spherical and nearly spherical particles, so long as

there are no irregular or sharp edges that would likely
cause attrition during handling or fluidization.

Conventionally, an abrasion resistant coating of
silica is used to make these spheroidal particles (or
5   microspheres) attrition resistant. U.S. Patent
4,769,477 teaches such an abrasion resistant coating
which is contemplated for potential use within the
confines of this invention without departing from the
spirit thereof. Commonly a silica coating is applied by
10   (a) forming a slurry comprised of catalyst or catalyst
precursor particles dispersed in an aqueous silicic acid
solution equivalent to a weight of SiO_2 not exceeding
about 6% by weight, the relative amounts of the
particles and silicic acid chosen so that the weight of
15   the SiO_2 formed is about 3-15% of the total weight of
the particles and the SiO_2, (b) spray drying the slurry
to form porous microspheres of attrition resistant
catalyst or catalyst precursor and (c) calcining the
spray dried microspheres at an elevated temperature
20   which is below the temperature which is substantially
deleterious to the catalyst, to produce attrition
resistant SiO_2 coated catalyst. Preferably, the silicic
acid is polysilicic acid having an equivalent
concentration of SiO_2 not exceeding about 5% by weight;
25   the catalyst or catalyst precursor particles are less
than about 10 μm in diameter; the microporous spheroidal
particles produced by spray drying have diameters of
from about 10 μm to about 300 μm, and the relative
amounts of particles to be spray dried and SiO_2 are
30   chosen so that the weight of the SiO_2 is about 5-12% of
the total weight of the particles and the SiO_2. It is
preferred that the size of the particles used in step
(a) above are from about 0.5 μm to about 10 μm and most
preferably from about 0.5 μm to about 3 μm.

The catalyst of the invention can be utilized
advantageously with regard to conversion and selectivity
in the wide variety of conventional techniques and
reactor configurations employed to conduct the vapor
5   phase oxidation of alkane hydrocarbons, particularly
n-butane to maleic anhydride. For example, the
conversion can be conducted in a fixed-bed reactor,
whereby the catalyst particles are maintained in a fixed
position and are contacted with alkane hydrocarbon and
10   oxygen in appropriate amounts, in the presence of one or
more inert diluent gases. The greatest advantages of
using the catalyst of this invention are realized when
the conversion of n-butane to maleic anhydride is
carried out in a recirculating solids reactor, such as
15   that described in U.S. Patent 4,668,802. This patent
discloses an improved process for the selective vapor
phase oxidation of n-butane to maleic anhydride over a
VPO catalyst, whereby the amount of oxygen in the feed
gas to the VPO catalyst is limited to less than the
20   stoichiometric amount required for the total amount of
n-butane converted in the process. The reduced catalyst
resulting from the oxidation is separated from the
gaseous product stream; and is reoxidized, optionally in
a separate reaction zone, before being contacted with
25   n-butane.
         While the present invention is not bound by theory
of, it is believed that the increased oxygen capacity of
the catalyst of this invention, selective to maleic
anhydride, allows this catalyst to effectively catalyze
30   high conversion to maleic anhydride, even under
conditions where the catalyst is completely reduced or
is the only source of oxygen for n-butane. This
behavior is contrasted with prior art catalysts and
promoted catalysts, such as that described in U.S.
35   Patent 4,442,226, wherein the VPO or promoted VPO

catalysts are sensitive to the partial pressure of
oxygen with respect to their catalytic activity and it
is recommended that the partial pressure of oxygen in
the feed by maximized within the limits of safe
5   operability. Use of the catalyst of the present
invention, consequently, provides advantages in safety
of operation as well as conversion, because one can
operate at levels of oxygen in the feed which are well
outside the explosive range of conventionally required
10 butane/oxygen/inert gas mixtures.

        Catalysts used in most oxidation systems can
comprise particles in the approximate size range 100-325
mesh (U.S. Sieve Series). The desired particle size
distribution for the catalyst of the present invention
15 may also be achieved by spray drying slurries of the
catalyst precursor at appropriate concentrations. To
enhance attrition resistance, variable amounts of
support, such as silica, can be incorporated into the
fluid-bed catalyst system by addition of colloidal
20 silica sol, for example, as one of the Ludox® colloidal
silica compositions commercially available from
E. I. du Pont de Nemours and Company, Wilmington,
Delaware, or a very fine silica powder, such as one of
the Cab-O-Sil® fumed silica commercially available from
25 Cabot Corporation, Tuscoloa, Illinois.

                              EXAMPLES

        The formula listed for each of Examples A, 1, 4,
11, 20, 21, 25, and 26 are exact due to the X-ray
crystallographic date presented. For the remainder of
30 the examples, formula I is used. However, these
Examples could also be represented by formula II, III,
or IV since structure studies have not been completed.

EXAMPLE 1

Preparation of $(V_{0.9}Sb_{0.05}Fe_{0.05}O)_2P_2O_7$

A 3 liter round bottom flask was equipped with an
addition funnel, mechanical stirrer and a reflux

5   condenser. For the duration of the reflux, nitrogen gas
was used to purge the apparatus. In an inert atmosphere
drybox containing nitrogen gas, 81.85 g of air
micronized vanadium pentoxide (Aldrich Chemicals,
Milwaukee, WI) was added to the round bottom flask.

10   8.11 g of anhydrous iron (III) chloride (Johnson,
Matthey – Alfa Chemicals, Ward Hill, MA) and 17.06 g of
antimony (III) butoxide (JM, Alfa Chemicals) were then
added. To this mixture, 1034 ml of isobutyl alcohol
(anhydrous, Aldrich Chemicals) and 95 ml of benzyl

15   alcohol (anhydrous, Aldrich Chemicals) were added. The
round bottom flask was then stoppered and brought
outside of the drybox. Anhydrous phosphoric acid was
prepared in the inert atmosphere dry box by mixing
85.8 g of 85+ % phosphoric acid (J.T. Baker and Co.,

20   Phillipsburg, NJ) with 33.2 g of phosphorus pentoxide
(J.T. Baker). The anhydrous phosphoric acid was then
added to the addition funnel, brought outside of the
drybox, and attached to the round bottom flask.

The vanadium pentoxide and alcohols were held at

25   reflux temperatures for one hour. Anhydrous phosphoric
acid was then added dropwise over a period of two hours.
Following this procedure, the reflux continued for a
period of fifteen additional hours. The precipitated
solids were then filtered in a buchner funnel and dried

30   in flowing nitrogen at 80-125°C for a period of 16 hours
to yield the catalyst precursor.

Following this procedure, the precursor was
directly calcined and activated in a small, 4 cm
fluidized bed reactor. Prior to the activation, fine

35   particles were sieved out by using a 400 mesh screen.

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The calcination/activation procedure generated the active catalyst phase by subjecting the precursor to the thermal conditions detailed below:

                25-390°C in air
5   390°C 1 hour in air
                390°C 1 hour in 1.5% butane/air
                390-460°C 20 minutes in 1.5% butane/air
                460-460°C 18 hours in 1.5% butane/air
                460-420°C in 1.5% butane air
10   420-360°C in 1.5% butane/air
                360°C-25°C in N_2

The resulting catalyst was analyzed by Scanning Transmission Electron Microscopy (STEM) and High Resolution Transmission Electron Microscopy (HREM) using
15 a commercially available Philips CM30 Super Twin HREM/STEM system operated at 300 keV for atomic scale imaging and high spatial resolution chemical composition analysis with the energy dispersive X-ray analyzer (EDX) and a STEM probe size of about 5 nanometers. The
20 catalyst sample was supported on a carbon-filmed microscope grid. Chemical analyses spectra were obtained from a large number of crystals and from a number of regions within each crystal. The data showed that Fe and Sb cations were homogeneously distributed.
25 The corresponding HREM lattice images showed regular periodicity with lattice lines extending directly to the surface with no evidence of an amorphous surface phase, line dislocations or stacking defects. The HREM/STEM data supported the formation of a solid solution in this
30 catalyst.

EXAMPLE 2

Preparation of $(V_{0.98}Sb_{0.01}Fe_{0.01}O)_2P_2O_{7\pm\delta}$

A 3 liter round bottom flask was equipped with an addition funnel, mechanical stirrer and a reflux
35 condenser. For the duration of the reflux, nitrogen gas

was used to purge the apparatus. In an inert atmosphere
drybox containing nitrogen gas, 89.12 g of air
micronized vanadium pentoxide (Aldrich Chemicals,
Milwaukee, WI) was added to the round bottom flask.
5   1.62 g of anhydrous iron (III) chloride (Johnson,
Matthey - Alfa Chemicals, Ward Hill, MA) and 3.41 g of
antimony (III) butoxide (JM, Alfa Chemicals) were then
added. To this mixture, 1000 ml of isobutyl alcohol
(anhydrous, Aldrich Chemicals) and 95 ml of benzyl
10 alcohol (anhydrous, Aldrich Chemicals) were added. The
round bottom flask was then stoppered and brought
outside of the drybox. Anhydrous phosphoric acid was
prepared in the inert atmosphere drybox by mixing 85.8 g
of 85+ % phosphoric acid (J.T. Baker and Co.,
15 Phillipsburg, NJ) with 33.2 g of phosphorus pentoxide
(J.T. Baker). The anhydrous phosphoric acid was then
added to the addition funnel, brought outside of the
drybox, and attached to the round bottom flask.
    The vanadium pentoxide and alcohols were held at
20 reflux temperatures for one hour. Anhydrous phosphoric
acid was then added dropwise over a period of two hours.
Following this procedure, the reflux continued for a
period of fifteen additional hours. The precipitated
solids are then filtered in a buchner funnel and dried
25 in flowing nitrogen at 125°C for a period of 16 hours.
    Following this procedure, the precursor was
directly calcined and activated in a small, 4 cm
fluidized bed reactor, to generate the active catalyst
phase by subjecting the precursor to the thermal
30 conditions detailed below:
            25-390°C in air
            390°C 1 hour in air
            390°C 1 hour in 1.5% butane/air
            390-460°C 20 minutes in 1.5% butane/air
35   460-460°C 18 hours in 1.5% butane/air

460-420°C in 1.5% butane air

420-360°C in 1.5% butane/air

360°C-25°C in N_2

Prior to the activation, fine particles were sieved out

5   by using a 400 mesh screen.

EXAMPLES 3-5

Preparation of $(V_{1-x-y}Sb_xFe_yO)_2P_2O_{7\pm\delta}$

The procedure described in Example 2 was used to prepare additional catalysts. The cation sources shown

10   in Table I were employed in the molar ratios shown. The formula of the catalysts produced were

$(V_{0.8}Sb_{0.1}Fe_{0.1}O)_2P_2O_{7\pm\delta}$, $(V_{0.9}Sb_{0.025}Fe_{0.075}O)_2P_2O_7$, and

$(V_{0.9}Sb_{0.075}Fe_{0.025}O)_2P_2O_{7\pm\delta}$.

EXAMPLE 6

15   ### Preparation of $(V_{0.9}Sb_{0.05}Fe_{0.05}O)_2P_2O_{7\pm\delta}$

A procedure similar to that of Example 1 was used. A 3 liter round bottom flask was equipped with an addition funnel, mechanical stirrer and a reflux condenser. For the duration of the reflux, nitrogen gas

20   was used to purge the apparatus. Vanadium pentoxide was air micronized to prior to use. In an inert atmosphere drybox containing nitrogen gas, 89.89 g of vanadium pentoxide (Aldrich Chemicals, Milwaukee, WI) was added to the round bottom flask. 8.91 g of anhydrous iron

25   (III) chloride (Johnson, Matthey - Alfa Chemicals, Ward Hill, MA) and 16.45 g of antimony pentachloride (anhydrous) (JM, Alfa Chemicals) were then added. To this mixture, 1034 ml of isobutyl alcohol (anhydrous, Aldrich Chemicals) and 95 ml of benzyl alcohol

30   (anhydrous, Aldrich Chemicals) were added. The round bottom flask was then stoppered and brought outside of the drybox. Anhydrous phosphoric acid was prepared in the inert atmosphere drybox by mixing 88.79 g of 85+ % phosphoric acid (J.T. Baker and Co., Phillipsburg, NJ)

35   with 33.2 g of phosphorus pentoxide (J.T. Baker). The

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anhydrous phosphoric acid was then added to the addition
funnel, brought outside of the drybox, and attached to
the round bottom flask.

The vanadium pentoxide and alcohols were held at
5   reflux temperatures for one hour. Anhydrous phosphoric
acid was then added dropwise over a period of two hours.
Following this procedure, the reflux continued for a
period of fifteen additional hours. The precipitated
solids were then filtered in a buchner funnel and dried
10 in flowing nitrogen at 125°C for a period of 16 hours to
yield the catalyst precursor.

Following this procedure, the precursor was
directly calcined and activated in a small, 4 cm
fluidized bed reactor, to generate the active catalyst
15 phase by subjecting the precursor to the thermal
conditions detailed below:

25-390°C in air
390°C 1 hour in air
390°C 1 hour in 1.5% butane/air
20   390-460°C 20 minutes in 1.5% butane/air
460-460°C 18 hours in 1.5% butane/air
460-420°C in 1.5% butane air
420-360°C in 1.5% butane/air
360°C-25°C in N_2

25 Prior to the activation, fine particles were sieved out
by using a 400 mesh screen.

EXAMPLE 7

Preparation of $(V_{0.9}Sb_{0.05}Fe_{0.05}O)_2P_2O_{7\pm\delta}$

A procedure similar to that of Example 1 was used.
30 A 3 liter round bottom flask was equipped with an
addition funnel, mechanical stirrer and a reflux
condenser. For the duration of the reflux, nitrogen gas
was used to purge the apparatus. Vanadium pentoxide was
air micronized to prior to use. In an inert atmosphere
35 drybox containing nitrogen gas, 89.89 g of vanadium

17

pentoxide (Aldrich Chemicals, Milwaukee, WI) was added
to the round bottom flask. 8.91 g of anhydrous iron
(III) chloride (Johnson, Matthey - Alfa Chemicals, Ward
Hill, MA) and 18.73 g of antimony butoxide (JM, Alfa
5   Chemicals) were then added. To this mixture, 1034 ml of
isobutyl alcohol (anhydrous, Aldrich Chemicals) and
95 ml of benzyl alcohol (anhydrous, Aldrich Chemicals)
were added. The round bottom flask was then stoppered
and brought outside of the drybox. Anhydrous phosphoric
10   acid was prepared in the inert atmosphere drybox by
mixing 85.79 g of 85+ % phosphoric acid (J.T. Baker and
Co., Phillipsburg, NJ) with 33.2 g of phosphorus
pentoxide (J.T. Baker). The anhydrous phosphoric acid
was then added to the addition funnel, brought outside
15   of the drybox, and attached to the round bottom flask.
       The vanadium pentoxide and alcohols were held at
reflux temperatures for one hour. Anhydrous phosphoric
acid was then added dropwise over a period of two hours.
Following this procedure, the reflux continued for a
20   period of fifteen additional hours. The precipitated
solids were then filtered in a buchner funnel and dried
in flowing nitrogen at 125°C for a period of 16 hours to
yield the precursor catalyst.
       Following this procedure, the precursor was
25   directly calcined and activated in a small, 4 cm
fluidized bed reactor, to generate the active catalyst
phase by subjecting the precursor to the thermal
conditions detailed below:
                25-390°C in air
30   390°C 1 hour in air
                390°C 1 hour in 1.5% butane/air
                390-460°C 20 minutes in 1.5% butane/air
                460-460°C 18 hours in 1.5% butane/air
                460-420°C in 1.5% butane air

18

420-360°C in 1.5% butane/air

360°C-25°C in N_2

Prior to the activation, fine particles were sieved out by using a 400 mesh screen.

5   EXAMPLES 8-13

Preparation of $(V_{1-x-y}A_xB_yO)_2P_2O_{7\pm\delta}$

The procedure described in Example 7 was used to prepare additional catalysts. The cation sources were as shown in Table I and were used in the molar ratios

10   shown. The formula of the catalysts produced were $(V_{0.9}Sb_{0.05}Fe_{0.05}O)_2P_2O_{7\pm\delta}$, $(V_{0.8}Sb_{0.1}Fe_{0.1}O)_2P_2O_{7\pm\delta}$, $(V_{0.8}Sb_{0.15}Fe_{0.05}O)_2P_2O_{7\pm\delta}$, $(V_{0.9}Sb_{0.05}Cu_{0.05}O)_2P_2O_7$, $(V_{0.9}Sb_{0.05}Cu_{0.05}O)_2P_2O_{7\pm\delta}$, and $(V_{0.9}Sb_{0.05}Mn_{0.05}O)_2P_2O_{7\pm\delta}$.

EXAMPLE 14

15   Preparation of $(V_{0.8}Sb_{0.1}Mn_{0.1}O)_2P_2O_7$

An 8 liter round bottom flask was equipped with an addition funnel, mechanical stirrer and a reflux condenser. For the duration of the reflux, nitrogen gas was used to purge the apparatus. In an inert atmosphere

20   drybox containing nitrogen gas, 239.7 g of vanadium pentoxide (Aldrich Chemicals, Milwaukee, WI) was added to the round bottom flask. The vanadium pentoxide was then air micronized. 83.41 g of manganese (II) acetyl acetonate (Johnson, Matthey - Alfa Chemicals, Ward Hill,

25   MA) and 112.38 g of antimony (III) butoxide (JM, Alfa Chemicals) were then added. To this mixture, 3102 ml of isobutyl alcohol (anhydrous, Aldrich Chemicals) and 285 ml of benzyl alcohol (anhydrous, Aldrich Chemicals) were added. The round bottom flask was then stoppered and

30   brought outside of the drybox. Anhydrous phosphoric acid was prepared in the inert atmosphere dry box by mixing 257.37 g of 85+ % phosphoric acid (J.T. Baker and Co., Phillipsburg, NJ) with 99.6 g of phosphorus pentoxide (J.T. Baker). The anhydrous phosphoric acid

was then added to the addition funnel, brought outside
of the drybox, and attached to the round bottom flask.

   The vanadium pentoxide and alcohols were held at
reflux temperatures for one hour. Anhydrous phosphoric

5 acid was then added dropwise over a period of two hours.
Following this procedure, the reflux continued for a
period of fifteen additional hours. The precipitated
solids are then filtered in a buchner funnel and dried
in flowing nitrogen at 125°C for a period of 16 hours to

10 yield the catalyst precursor.

   Following this procedure, the precursor was
directly calcined and activated in a small, 4 cm
fluidized bed reactor, to generate the active catalyst
phase by subjecting the precursor to the thermal

15 conditions detailed below:

          25-390°C in air
          390°C 1 hour in air
          390°C 1 hour in 1.5% butane/air
          390-460°C 20 minutes in 1.5% butane/air
20   460-460°C 18 hours in 1.5% butane/air
          460-420°C in 1.5% butane air
          420-360°C in 1.5% butane/air
          360°C-25°C in N_2

Prior to the activation, fine particles were sieved out
25 by using a 400 mesh screen.

                    EXAMPLES 15-17

          Preparation of $(V_{1-x-y}A_xB_yO)_2P_2O_{7\pm\delta}$

   The procedure described in Example 7 was used to
prepare additional catalysts. The cation sources were
30 as shown in Table I and were used in the molar ratios
shown. The formula of the catalysts produced were
$(V_{0.9}Sb_{0.05}Al_{0.05}O)_2P_2O_{7\pm\delta}$, $(V_{0.6}Sb_{0.2}Al_{0.2}O)_2P_2O_{7\pm\delta}$, and
$(V_{0.8}Sb_{0.05}Li_{0.1}Fe_{0.05}O)_2P_2O_{7\pm\delta}$.

EXAMPLE 18

Preparation of $(V_{0.81}Sb_{0.09}Ce_{0.10})_2P_2O_{7\pm\delta}$

The procedure described in Example 14 were used.
The cation sources were as shown in Table I and were

5   used in the molar ratios shown. The formula of the
catalyst produced was $(V_{0.81}Sb_{0.09}Ce_{0.10})_2P_2O_{7\pm\delta}$.

EXAMPLE 19

Preparation of $(V_{0.9}Sb_{0.05}Ni_{0.05}O)_2P_2O_{7\pm\delta}$

The procedure described in Example 7 was used. The

10 cation sources were as shown in Table I and were used in
the molar ratios shown. The formula of the catalyst
produced was $(V_{0.09}Sb_{0.05}Ni_{0.05}O)_2P_2O_{7\pm\delta}$.

EXAMPLE 20

Preparation of $(V_{0.9}Sb_{0.05}Cr_{0.05}O)_2P_2O_7$

15   The procedure described in Example 2 was used. The
cation sources were as shown in Table I and were used in
the molar ratios shown. The formula of the catalyst
produced was $(V_{0.9}Sb_{0.05}Cr_{0.05}O)_2P_2O_{7\pm\delta}$.

EXAMPLE 21

Preparation of $(V_{0.9}Bi_{0.05}Sb_{0.05}O)_2P_2O_7$

20

A procedure similar to that described in Example 6
was used. A 3 liter round bottom flask was equipped
with an addition funnel, mechanical stirrer and a reflux
condenser. For the duration of the reflux, nitrogen gas

25 was used to purge the apparatus. In an inert atmosphere
drybox containing nitrogen gas, 89.89 g of vanadium
pentoxide (Aldrich Chemicals, Milwaukee, WI) was added
to the round bottom flask. The vanadium pentoxide was
then air micronized. 17.32 g of $BiCl_3$ (Johnson, Matthey

30 - Alfa Chemicals, Ward Hill, MA) and 16.43 g of $SbCl_5$
(JM, Alfa Chemicals) were then added. To this mixture,
1034 ml of isobutyl alcohol (anhydrous, Aldrich
Chemicals) and 95 ml of benzyl alcohol (anhydrous,
Aldrich Chemicals) were added. The round bottom flask

35 was then stoppered and brought outside of the drybox.

21

Anhydrous phosphoric acid was prepared in the inert
atmosphere dry box by mixing 88.8 g of 85+ % phosphoric
acid (J.T. Baker and Co., Phillipsburg, NJ) with 33.2 g
of phosphorus pentoxide (J.T. Baker). The anhydrous
5   phosphoric acid was then added to the addition funnel,
brought outside of the drybox, and attached to the round
bottom flask.

The vanadium pentoxide and alcohols were held at
reflux temperatures for one hour. Anhydrous phosphoric
10   acid was then added dropwise over a period of two hours.
Following this procedure, the reflux continued for a
period of fifteen additional hours. The precipitated
solids are then filtered in a buchner funnel and dried
in flowing nitrogen at 125°C for a period of 16 hours to
15   yield the catalyst precursor.

Following this procedure, the precursor was
directly calcined and activated in a small, 4 cm
fluidized bed reactor, to generate the active catalyst
phase by subjecting the precursor to the thermal
20   conditions detailed below:

       25-390°C in air
       390°C 1 hr in air
       390°C 1 hour in 1.5% butane/air
       390-460°C 20 minutes in 1.5% butane/air
25   460-460°C 18 hours in 1.5% butane/air
       460-420°C in 1.5% butane air
       420-360°C in 1.5% butane/air
       360°C-25°C in N_2

Prior to the activation, fine particles were sieved out
30   by using a 400 mesh screen.

EXAMPLE 22

Preparation of $(V_{0.9}Bi_{0.05}Sb_{0.05}O)_2P_2O_{7\pm\delta}$

The procedure described in Example 21 was used.
The cation sources were as shown in Table I and were

used in the molar ratios shown. The formula of the
catalyst produced was $(V_{0.9}Bi_{0.05}Sb_{0.05}O)_2P_2O_{7\pm\delta}$.

EXAMPLES 23-28

Preparation of $(V_{1-x-y}A_xB_yO)_2P_2O_{7\pm\delta}$

5   The procedure described in Example 7 was used. The
cation sources were as shown in Table I and were used in
the molar ratios shown. The formula of the catalysts
produced were $(V_{0.9}Bi_{0.05}Sb_{0.05}O)_2P_2O_{7\pm\delta}$,
$(V_{0.9}Bi_{0.05}Sb_{0.05}O)_2P_2O_{7\pm\delta}$, $(V_{0.9}Sb_{0.05}Sn_{0.05}O)_2P_2O_7$,

10    $(V_{0.9}Sb_{0.05}Ga_{0.05}O)_2P_2O_7$, $(V_{0.9}Sb_{0.05}Co_{0.05}O)_2P_2O_{7\pm\delta}$, and
$(V_{0.8}Sb_{0.1}Co_{0.1}O)_2P_2O_{7\pm\delta}$.

TABLE I

Example No.	Cation Substituents B,A	Mole Ratio of V:B:A	Sources of cation substituent B,A
2	Fe,Sb	0.98:0.01:0.01	$FeCl_3$, $Sb(OC_4H_9)_3$
3	Fe,Sb	0.8:0.1:0.1	$FeCl_3$, $Sb(OC_4H_9)_3$
4	Fe,Sb	0.9:0.075:0.025	$FeCl_3$, $Sb(OC_4H_9)_3$
5	Fe,Sb	0.9:0.025:0.075	$FeCl_3$, $Sb(OC_4H_9)_3$
6	Fe,Sb	0.9:0.05:0.05	$FeCl_3$, $SbCl_5$
7	Fe,Sb	0.9:0.05:0.05	$FeCl_3$, $Sb(OC_4H_9)_3$
8	Fe,Sb	0.9:0.05:0.05	Iron(III)pentanedionate, $Sb(OC_4H_9)$
9	Fe,Sb	0.8:0.1:0.1	Iron(III)pentanedionate, $Sb(OC_4H_9)$
10	Fe,Sb	0.8:0.05:0.15	$FeCl_3$,$Sb(OC_4H_9)_3$
11	Cu,Sb	0.9:0.05:0.05	Copper oxide, $Sb(OC_4H_9)_3$
12	Cu, Sb	0.9:0.05:0.05	Cu(II)2,4 pentanedionate dihydrate, $Sb(OC_4H_9)_3$
13	Mn,Sb	0.9:0.05:0.05	Manganese(II) acetyl-acetonate, $Sb(OC_4H_9)_3$
14	Mn,Sb	0.8:0.1:0.1	Manganese(II) acetyl-acetonate, $Sb(OC_4H_9)_3$
15	Al,Sb	0.9:0.05:0.05	Aluminum isopropoxide, $Sb(OC_4H_9)_3$
16	Al,Sb	0.6:0.2:0.2	Aluminum isopropoxide, $Sb(OC_4H_9)_3$

17	Li,Fe,Sb	0.8:0.1:0.05:0.05	Lithium benzoate, FeCl3, $Sb(OC_4H_9)_3$
18	Ce,Sb	0.81:0.1:0.09	CeO_2, $Sb(OC_4H_9)_3$
19	Ni,Sb	0.9:0.05:0.05:1	Nickel(II)pentanedionate, $Sb(OC_4H_9)_3$
20	Cr,Sb	0.9:0.05:0.05	Chromium(III) acetate hydroxide, $Sb(OC_4H_9)_3$
21	Bi,Sb	0.9:0.05:0.05	$BiCl_3$, $SbCl_5$
22	Bi,Sb	0.9:0.05:0.05	$BiCl_3$, $Sb(OC_4H_9)_3$
23	Bi,Sb	0.9:0.05:0.05	$BiCl_3$, $SbCl_5$
24	Bi,Sb	0.9:0.05:0.05	Bismuth 2-ethylhexanoate, $Sb(OC_4H_9)_3$
25	Sn,Sb	0.9:0.05:0.05	Tin(II)ethoxide, $Sb(OC_4H_9)_3$
26	Ga,Sb	0.9:0.05:0.05	$GaCl_3$, $Sb(OC_4H_9)_3$
27	Co,Sb	0.9:0.05:0.05	Co(II)2,4 pentanedionate, $Sb(OC_4H_9)_3$
28	Co,Sb	0.8:0.1:0.1	Co(II)2,4 pentanedionate, $Sb(OC_4H_9)_3$

COMPARATIVE EXAMPLE A
Preparation of $(VO)_2P_2O_7$

The procedure of Example 7 was followed except that no antimony butoxide nor iron chloride were used. The
5   formula of the catalyst produced was $(VO)_2P_2O_7$.

COMPARATIVE EXAMPLE B
Preparation of $(V_{0.9}Cr_{0.1}O)_2P_2O_7$

The procedure of Example 2 was followed except that Chromium(III) acetate hydroxide alone was used instead
10   of antimony butoxide and iron chloride. The formula of the catalyst produced was $(V_{0.9}Cr_{0.1}O)_2P_2O_7$.

COMPARATIVE EXAMPLE C
Preparation of $(V_{0.9}Fe_{0.05}Cr_{0.05}O)_2P_2O_7$

The procedure of Example 14 was followed except
15   that Chromium(III) acetate hydroxide was used instead of manganese acetyl acetoate. The formula of the catalyst produced was $(V_{0.9}Fe_{0.05}Cr_{0.05}O)_2P_2O_7$.

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EXAMPLE 29
Conversion/Selectivity data in pulsed micro-reactor

The catalysts in accordance with this invention
from Example 1, Comparative Example A, Comparative

5　Example B and Comparative Example C prepared above were
utilized in the pulsed microreactor described below to
catalyze the conversion of butane to maleic anhydride.

Pulse reactor evaluation of the catalysts was
carried out by injecting 0.05 ml pulses of butane by

10　means of a gas sampling valve contained in an oven at
170°C into a stream of helium flowing at 10 ml/min that
passed over 0.5 grams of catalyst in a reactor made from
1/8" (3.2 mm) tubing and heated in a tube furnace to
380°C. The effluent of the reactor passed through a

15　thermal conductivity detector and then through a sample
loop. When the pulse was in the sample loop, as
determined by the thermal conductivity detector, it was
injected into a gas chromatograph for analysis of the
reaction products. Butane pulses were passed over the

20　catalyst every 10 min, with alternate pulses being
analyzed. Butane conversions and selectivities to
maleic anhydride with successive butane pulses are shown
in Figures 1 and 2. These were calculated by the
following formulas

25　　　　　Butane conversion = butane in product/butane
in feed.

Selectivity to maleic anhydride = moles maleic anhydride
produced/moles butane reacted.

Pulsed microreactor evaluations of these catalysts

30　showed differences between substituted vanadium
phosphates and their parent compounds as shown in
Figures 1 and 2. Figure 1 shows that the catalyst was
reduced with successive butane pulses. The catalyst of
Example 1 maintained conversion levels relative to the

35　Comparative Example A, Comparative Example B and

Comparative Example C catalyst. Figure 2 showed that as
the catalyst was reduced with successive butane pulses,
the catalyst of Example 1 maintained selectivity
relative to the Comparative Example A, Comparative
5   Example B and Comparative Example C catalyst.

COMPARATIVE EXAMPLE D
Preparation of $(VO)_2P_2O_7$ with spray drying

Vanadium phosphate precursor, prepared as described
in Example 7 (correcting for the stoichiometry by
10   replacing Fe and Sb with an equimolar amount of vanadium
to make a VPO catalyst), was repeated 14 times to yield
14 combined batches. This precursor was air micronized
to a particle size less than 5 microns in diameter.
2000 g of this precursor was then slurried in 5% (wt %
15   as SiO_2) of polysilicic acid (PSA). The 5% PSA was
prepared by mixing 1014 g of sodium silicate with 5000 g
of H_2O. The Na was then removed by combining with DOWEX
HCR-W2 sulfonic acid resin (Dow Chemicals, Midland
Michigan). The appropriate amount of PSA was used
20   fresh. The time of contact of the slurry with the
polysilicic acid was kept to less than about 30 minutes.
The catalyst slurry was then spray dried to produce a
final catalyst composition containing 10 wt % SiO_2.

This slurry was then poured through a cheesecloth,
25   to filter out any very large clumps of catalyst, and
then pumped into a commercially available spray dryer
(Bowen Dryer, available from Bowen Engineering
Corporation, Columbia, Maryland). This spray dryer is a
4 ft diameter, 8 ft straight end electrically fired
30   dryer. Typical spray drying conditions include a feed
rate of 160 m./min, an inlet temperature of 376°C to the
dryer and outlet temperatures of 160-170°C. The
catalyst was then calcine activated in accordance with
the procedure of Example 1.

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EXAMPLE 30
Preparation of $(V_{0.9}Sb_{0.05}Fe_{0.05}O)_2P_2O_{7\pm\delta}$ with spray drying

The procedure of Comparative Example D was followed except that the catalyst precursor used was prepared
5   according to Example 7.

EXAMPLE 31
Preparation of $(V_{0.8}Sb_{0.1}Fe_{0.1}O)_2P_2O_{7\pm\delta}$ with spray drying

The procedure of Example 7 was followed for the preparation of the precursor, correcting for the
10   stoichiometry of iron and antimony. The resulting catalyst precursor was then treated in accordance with the procedure of Comparative Example D, except that 350 g of micronized precursor was slurried with 700.4 g of 5% polysilicic acid prior to spray drying.

15   ## EXAMPLE 32
Preparation of $(V_{0.8}Sb_{0.05}Li_{0.1}Fe_{0.05}O)_2P_2O_{7\pm\delta}$
with spray drying

The procedure of Example 31 was followed except for correcting for the stoichiometry of the catalyst
20   precursor. Lithium benzoate was used for the source of lithium.

EXAMPLE 33
Preparation of $(V_{0.9}Sb_{0.05}Mn_{0.05}O)_2P_2O_{7\pm\delta}$ with spray drying

The procedure of Example 31 was followed except for
25   correcting for the stoichiometry of the catalyst precursor. Manganese acetate and antimony butoxide were the sources of Mn and Sb.

EXAMPLE 34
Preparation of $(V_{0.6}Sb_{0.2}Al_{0.2}O)_2P_2O_{7\pm\delta}$ with spray drying

30   The procedure of Example 16 was followed to prepare two batches of the precursor which were subsequently micronized. They were spray dried and then calcined/activated in accordance with the procedure of Comparative Example 31.

27

EXAMPLE 35
Preparation of $(V_{0.9}Sb_{0.05}Cu_{0.05}O)_2P_2O_{7+\delta}$ with spray drying

The procedure of Example 11 was followed to prepare
two batches of the precursors which were subsequently
5   micronized. The precursor was spray dried and then
calcined/activated in accordance with the procedure of
Comparative Example 31.

EXAMPLE 36
Preparation of $(V_{0.9}Fe_{0.1})_2P_{1.8}Bi_{0.2}O_{7+\delta}$ with spray drying

10   Two batches of the commercial precursor was
prepared using the 3 liter reflux apparatus described in
Example 7. The procedure used was similar to Example 7,
except for the reagents. 89.89 g of vanadium pentoxide,
17.82 g of iron trichloride (anhydrous), 77.93 g of
15   bismuth 2-ethylhexanoate were used. The amount of
phosporic acid and phosphorus pentoxide used were 29.88
and 29.88 g, respectively.

Two batches of this precursor was prepared, spray
dried and calcined/activated according to the procedure
20   of Example 31.

EXAMPLE 37
Conversion/Selectivity data in fixed bed-reactor

A fixed bed micro-reactor was used to evaluate the
catalysts from Comparative Example D and Examples 30-36,
25   inclusive. The microreactor consisted of a 40.64 cm by
0.64 cm stainless steel tube enclosed by an aluminum
sheath (3.12 cm thick, to assist in minimizing thermal
gradients) which itself was enclosed in a tube furnace.
The reactor was mounted vertically with the direction of
30   the of gas flow from top to bottom. Pressure gauges
were mounted near both the entrance and exit of the
reactor to monitor pressure changes. A bypass valve
installed near the reactor entrance allowed the entering
gas stream to pass through either the reactor or to
35   bypass the reactor and pass directly to the sampling

valve system, allowing analysis of the reactor feed
gases prior to reaction. Also, a T connection at the
top of the reactor allowed a thermocouple to be mounted
such that it monitored the temperature at the entrance
5   to the packed catalyst bed. Commercially available mass
flowmeters (Tylan Model FC-260) of ranges 0-100 and
0-10 cc/minute, respectively, fed the reactor. The
heated exit gas stream (200°C) passed through a heated
sampling valve allowing the selection of a gas sample
10 (250 μl) of the stream for analysis by gas-liquid
chromatography (GLC), using a commercially availablke
instrument (Gow-Mac Series 740P FID GLC). The GLC was
used to analyze for butane and for products to maleic
anhydride, acetic acid and acrylic acid.

15   The pseudo-first order rate constant, k, given for
the disappearance of butane in the Table was obtained by
fitting the reactor data to a classical first order rate
expression:

$$d[butane]/dt = -k[butane]$$

20 $$d(xo - x)/dt = -k(xo - x)$$

where xo = initial conc. of butane

x = portion of butane reacted

Integrating this expression gave the concentration
of butane exiting the reactor as a function of contact
25 time, t, in the reactor:

$$[exit\ butane] = xo - x = xo^{-kt}$$

In addition to describing the reaction rate of
butane with a catalyst, the rate constant k included
several other factors including the dependence of the
30 reaction rate on oxygen concentration (which remained
relatively constant under our conditions) and the
concentration of catalyst active sites (also assumed
constant).

Rate constants and selectivity at 40% conversion is
35 shown in Table 2.

TABLE 2

Spray Dried Catalysts

Example	Mole Ratio of V:A:B:P	k (sec)$^{-1}$	Selectivity at 40% conversion
D	1:0:0:~1	1.15	49
30	0.9:0.05:0.05:~1	1.18	74
31	0.8:0.1:0.1:~1	1.25	65
32	0.0.05:8:0.1:0.05:~1	0.53	46
33	0.9:0.05:0.05:~1	1.00	52
34	0.6:0.2:0.2:~1	0.66	19
35	0.9:0.05:0.05:~1	2.54	67
36	1.8:0.2:0.2:~1.8	0.63	15

EXAMPLE 38

X-ray diffraction

X-ray data were obtained at room temperature on the catalysts prepared in accordance with Examples 1, 4, 21, 20, 11, 25, 26 and Comparative Example A using a conventional commercially available diffractometer (Philips XRD 3600 powder diffractometer with CuKalpha radiation), using 0.02 C 2θ steps and 0.5 seconds count time per step. Cell parameters were refined with the aid of a least squared fitting program which corrected for random errors, as well as the systematic error effects of the diffractometer. All d-spacings were calculated on the basis of the CuKα1 line (1.5405 Å) (0.15405 nm) and included the systematic error corrections. The listed 2-theta values are uncorrected for the systematic errors. The x-ray diffraction data analyisis showed the activated catalysts in accordance with this invention closely resembled single phase β-(VO)$_2$P$_2$O$_7$, with substantially no trace of separate promoter phases.

The results are shown in Table 3.

TABLE 3

X-Ray Diffraction Data[*]

Example No.	a (Å)	b (Å)	c (Å)	V (Å^3)
A	9.59(1)	7.76(2)	16.59(1)	
1	9.68	7.76	16.63	1249
4	9.57	7.84	16.6	1245
21	9.57	7.77	16.55	1231
20	9.62	7.74	16.6	1236
11	9.59	7.82	16.55	1241
25	9.58	7.80	16.57	1238
26	9.6	7.76	16.56	1234

[*]1Å = 0.1 nm

COMPARATIVE EXAMPLE E

Preparation of $(VO)_2P_2O_7/SiO_2$ and Conditioning in Circulating Solids Reactor

The procedure of Comparative Example D was
followed, except that the catalyst was further
conditioned in a circulating solids reactor as described
in U.S. 4,668,802, wherein the amount of oxygen in the
feed gas to the catalyst was limited to less than the
stoichiometric amount required for the total amount of
n-butane converted in the process. The reduced catalyst
resulting from the oxidation was separated from the
gaseous product stream; and was reoxidized, optionally
in a separate reaction zone, before being contacted with
n-butane in a pulsed micro reactor as described in
Example 29.

Conversion and selectivity versus the number of
butane pulses is shown in Figures 3 and 4, respectively.

EXAMPLE 39

Preparation of $(V_{0.9}Fe_{0.05}Sb_{0.05}O)_2P_2O_{7\pm\delta}/SiO_2$ and Conditioning in Circulating Solids Reactor

The procedure of Example 30 was followed, except
that the catalyst was further conditioned in a

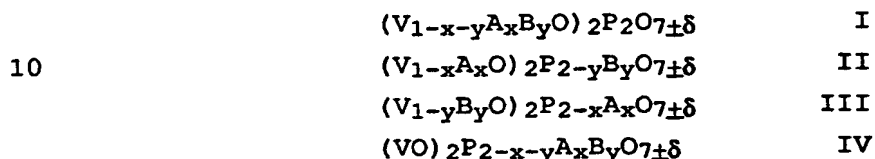circulating solids reactor in accordance with
Comparative Example D.

Conversion and selectivity versus the number of
butane pulses is shown in Figures 3 and 4, respectively.
5 It is seen from Figure 4 that the catalyst in accordance
with the invention (Example 39) maintained selectivity
relative to the Comparative Example D with successive
butane pulses.

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CLAIMS

What is claimed is:

1.   An improved vanadium phosphorus oxygen
catalyst for the oxidation of alkane hydrocarbons
wherein the improvement comprises the presence of two
promoters A and B in the catalyst, said catalyst
comprising a crystalline oxide of formula I through IV

$$(V_{1-x-y}A_xB_yO)_2P_2O_{7\pm\delta} \qquad \text{I}$$
$$(V_{1-x}A_xO)_2P_{2-y}B_yO_{7\pm\delta} \qquad \text{II}$$
$$(V_{1-y}B_yO)_2P_{2-x}A_xO_{7\pm\delta} \qquad \text{III}$$
$$(VO)_2P_{2-x-y}A_xB_yO_{7\pm\delta} \qquad \text{IV}$$

wherein

A is at least one cation selected from the
group consisting of Sb, As, and Bi;

B is at least one cation selected from the
group consisting of Ge, Sb, Pb, Al, Ga, Tl, Sc, V, Cr,
Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag,
Cd, La, Hf, W, Re, Os, Ir, Pt, Au, Ho, Be, Mg, Ca, Sr,
Ba, Ra, Li, Na, K, Rb, Cs, and the rare earths including
Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th,
Pa, and U;

δ is 0 to less than 0.5; and

x and y are as follows:

in formula I: $0.7 \geq x > 0$ for each A, $0.7 \geq y > 0$ for
                 each B, and $0.7 \geq (x+y) > 0$;

in formula II: $0.7 \geq x > 0$ for each A, and $1.0 \geq y > 0$
                 for each B;

in formula III: $1.0 \geq x > 0$ for each A, and $0.7 \geq y > 0$
                 for each B; and

in formula IV: $1.0 > x > 0$ for each A, $1.0 > y > 0$ for
                 each B, and $1 \geq (x+y) > 0$.

2.   The catalyst of Claim 1 wherein A is Sb.

3.   The catalyst of Claim 1 wherein B is selected from the group consisting of Fe, Cu, Mn, Al, Li, Ce, Ni, Cr, Bi, Sn, Ga, and Co.
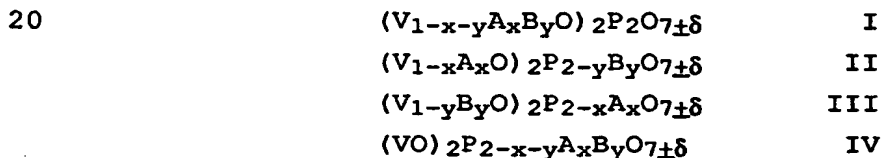
4.   The catalyst of Claim 2 wherein B is Fe.

5.   The catalyst of Claim 1 in the form of a solid solution.

6.   The catalyst of Claim 1 wherein, in the catalyst preparation, the promoters A and B are introduced into the reaction medium as inorganic salts.

7.   The catalyst of Claim 6 wherein, in the catalyst preparation, the promoters A and B are each independently introduced into the reaction medium as a salt selected from the group consisting of an acetate, alkoxide, anhydrous halide, and acetylacetonate.

8.   An improved process for the oxidation of n-butane to maleic anhydride using a vanadium phosphorus oxygen catalyst wherein the improvement comprises using a catalyst comprising a crystalline oxide of formula I through IV

$$(V_{1-x-y}A_xB_yO)_2P_2O_{7\pm\delta} \qquad I$$
$$(V_{1-x}A_xO)_2P_{2-y}B_yO_{7\pm\delta} \qquad II$$
$$(V_{1-y}B_yO)_2P_{2-x}A_xO_{7\pm\delta} \qquad III$$
$$(VO)_2P_{2-x-y}A_xB_yO_{7\pm\delta} \qquad IV$$

wherein

A is at least one cation selected from the group consisting of Sb, As, and Bi;

B is at least one cation selected from the group consisting of Ge, Sb, Pb, Al, Ga, Tl, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, La, Hf, W, Re, Os, Ir, Pt, Au, Ho, Be, Mg, Ca, Sr, Ba, Ra, Li, Na, K, Rb, Cs, and the rare earths including Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, Pa, and U;

δ is 0 to less than 0.5; and

x and y are as follows:

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in formula I: $0.7 \geq x > 0$ for each A, $0.7 \geq y > 0$ for
                  each B, and $0.7 \geq (x+y) > 0$;
in formula II: $0.7 \geq x > 0$ for each A, and $1.0 \geq y > 0$
                  for each B;
5   in formula III: $1.0 \geq x > 0$ for each A, and $0.7 \geq y > 0$
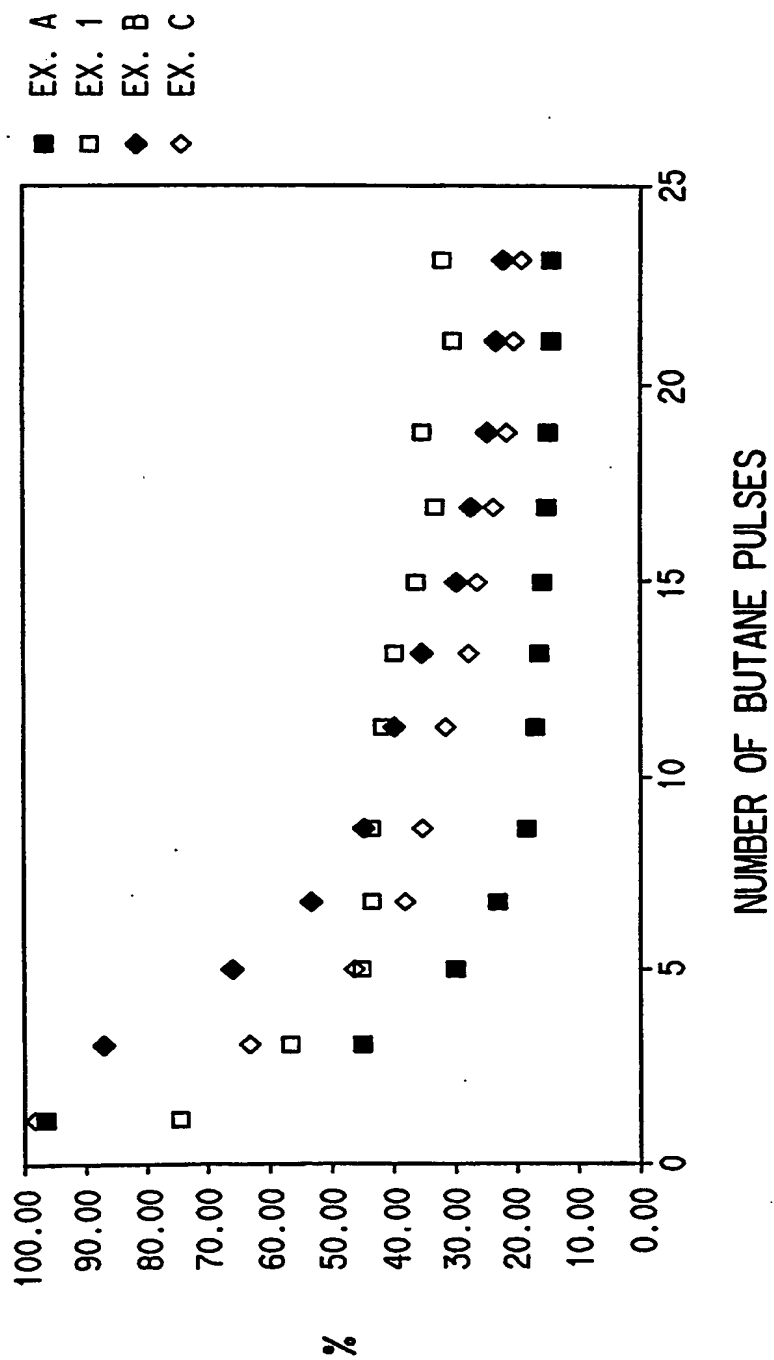   for each B; and
in formula IV: $1.0 > x > 0$ for each A, $1.0 > y > 0$ for
                  each B, and $1 \geq (x+y) > 0$.

    9.   The process of Claim 8 wherein the catalyst is
10   the only source of oxygen.

    10.   The process of Claim 8 wherein the oxidation
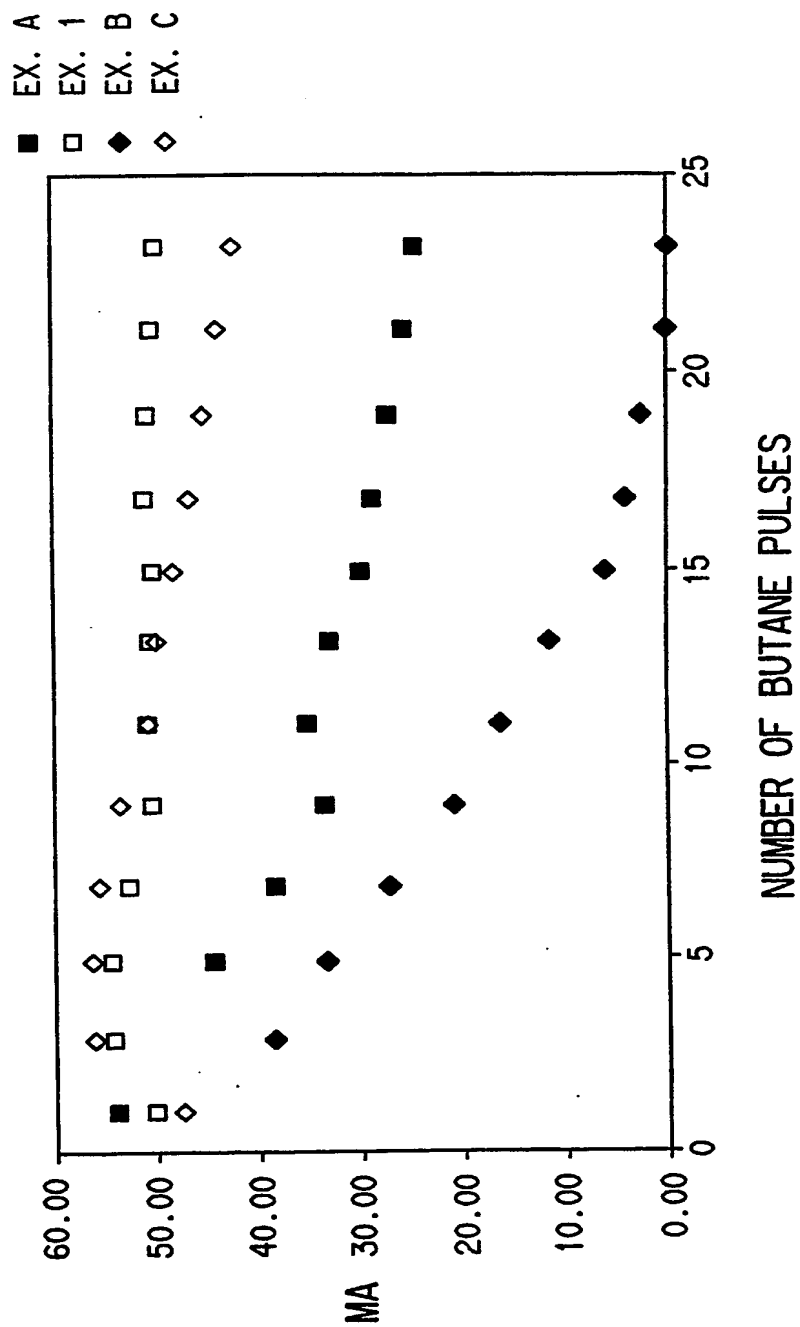is carried out in a recirculating solids reactor.

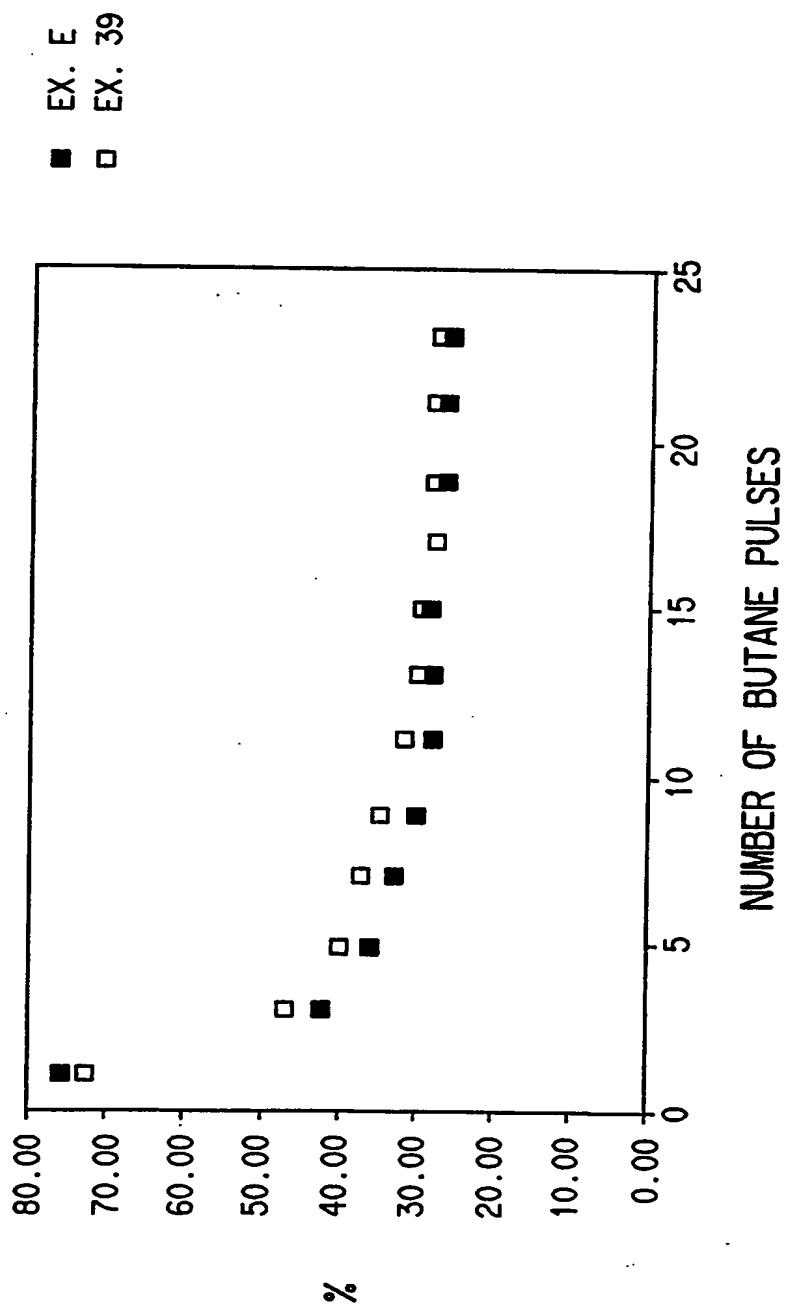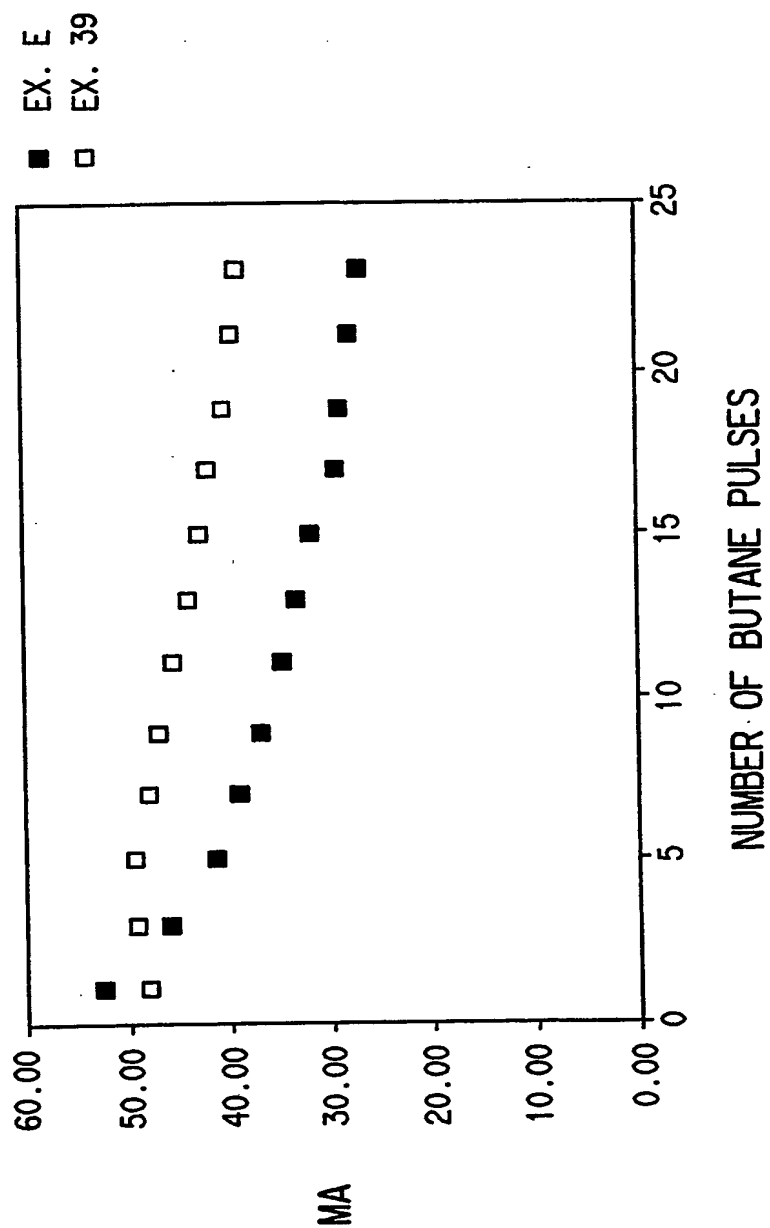# FIG.1

FIG.2

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FIG.3

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FIG. 4

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   B01J27/198   C07C51/215   C07C57/145

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   B01J   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 178 304 (EFENDIEV MEDZHID R O ET AL) 11 December 1979 see column 1, line 43 - line 62 see examples 1,12 see claims	1
X	EP,A,0 518 548 (STANDARD OIL CO OHIO) 16 December 1992 see page 1, line 10 - line 21 see claims	1
A	US,A,4 337 173 (OTAKE MASAYUKI) 29 June 1982 cited in the application	
A	US,A,4 442 226 (BITHER JR TOM A) 10 April 1984 cited in the application	

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[X] Further documents are listed in the continuation of box C.	[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
10 July 1995	1 3 -07- 1995

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 219 484 (BREMER NOEL J ET AL) 26 August 1980 -----	

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4178304	11-12-79	NONE		
EP-A-0518548	16-12-92	US-A-	5300682	05-04-94
		JP-A-	5178785	20-07-93
US-A-4337173	29-06-82	NONE		
US-A-4442226	10-04-84	US-A-	4371702	01-02-83
		CA-A-	1191831	13-08-85
		EP-A,B	0087118	31-08-83
		JP-C-	1706128	27-10-92
		JP-B-	3069577	01-11-91
		JP-A-	58150437	07-09-83
US-A-4219484	26-08-80	NONE		

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